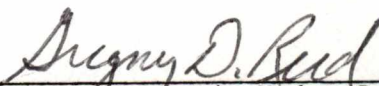


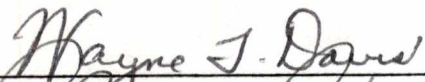
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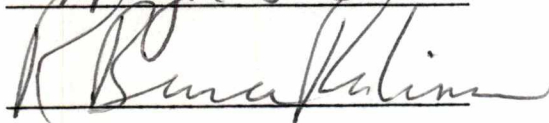
I am submitting herewith a thesis written by Ayoub V. Torkian entitled "Adsorption as a Mechanism Responsible for Increased FGD Efficiencies Due to Product Recycle." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.



Gregory D. Reed, Major Professor

We have read this thesis and
recommend its acceptance:





Accepted for the Council:



The Graduate School

ADSORPTION AS A MECHANISM RESPONSIBLE FOR INCREASED FGD
EFFICIENCIES DUE TO PRODUCT RECYCLE

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Ayoub V. Torkian

December 1983

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ABSTRACT

Tests were conducted on products generated at The University of Tennessee FGD pilot plant to study their adsorptive behavior. They were also tested for CaCO_3 content. Results of these bench-scale experiments were compared with pilot plant data. It was concluded that the increase in SO_2 removal efficiencies observed at the pilot plant due to product recycle could be due to adsorption of lime on the surface of products. It was also suggested that CaCO_3 may have a negative effect on the beneficial effects of product recycle.

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CHAPTER I

BACKGROUND

A. INTRODUCTION

Control of sulfur dioxide emissions has received increasingly more attention during the past ten years. Although SO_2 comes from many sources, power production from burning coal contributes up to 70 percent of the total man-made SO_2 emissions (Slack et al., 1975). Present trends of price increases for other fossil fuels will increase the consumption of coal, thus increasing the severity of the SO_2 problem.

Health effects of SO_2 on humans and animals are not certain. The Environmental Protection Agency (EPA) health effects monograph mentions that there are many uncertainties associated with effects of SO_2 on humans. Studies on animals suggest higher biological reactivities for sulfuric acid and certain sulfates than SO_2 (Federal Power Commission, 1977). On ecological effects, SO_2 gas reacts either photochemically or catalytically with other pollutants such as particulates forming sulfur trioxide, sulfuric acid, and various salts of sulfuric acid (Wark et al., 1981). Acid rain precipitation and the associated damages are frequently presumed to be related to SO_2 emissions. The Federal Power Commission (1977) had concluded that there was insufficient evidence to relate acid rain to SO_2 emissions from utility plants.

B. CONTROL ALTERNATIVES

1. Dilution

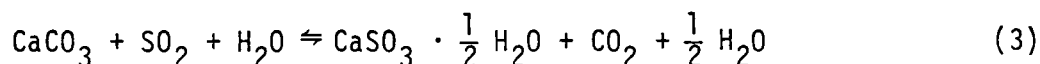
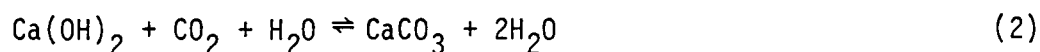
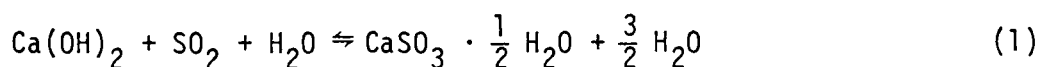
There are many ways to control ambient concentrations of SO_2 , one of which is diluting the effluent by allowing it more time to spread over wider areas. To achieve this goal taller stacks were constructed to allow more chance of dilution with air and less chance for plume bending back to the ground after leaving the stack. But since the total amount of SO_2 emitted results in increased concentrations over wider areas, EPA limits the SO_2 emission rate to $1.2 \text{ lb}/10^6 \text{ Btu}$ for coal-fired boilers (Federal Register, 1980).

2. Low-Sulfur Coal

Another approach is to use low-sulfur coal. Unfortunately, the cost of getting western coal (Wyoming and Montana) to the consumption sites does not favor its use. While approximately 62 percent of this coal is west of the Mississippi, 90 percent of the coal consuming utility power plants are located east of the Mississippi (Wark et al., 1981). Even though some of the transportation costs can be compensated since less pollution control equipment would be needed, many times transportation costs are such that use of high-sulfur coal is favored. Another factor to consider is that low-sulfur coal may contain 5 to 40 percent less energy (BTU) than low- or high-sulfur western coal. More coal used to get the same energy generally produces more ash, thus increasing the disposal cost.

3. Wet Lime/Limestone

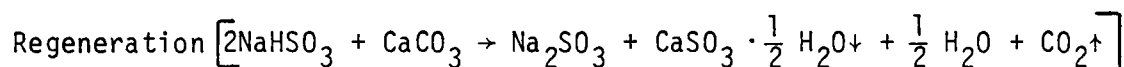
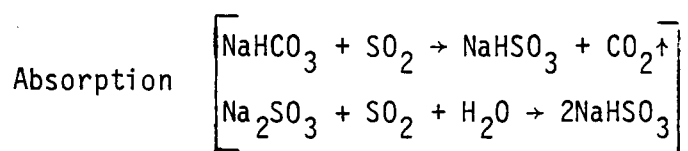
The wet lime scrubbing process was developed in the 1930s by Imperial Chemical Industries of England attaining SO₂ removal efficiencies of over 90 percent in pilot plant operation (Wark et al., 1981). Lime/limestone slurry scrubbing is presently the dominant commercial technology for flue gas desulfurization (FGD). The process involves absorption of SO₂ at 120-130°F and pH 5.5-6.0 by injecting water-based slurry of CaCO₃ and product solids. The following reactions are believed to occur (Getler, 1979):



Although the overall reactions as presented above are simple, the process chemistry as determined in a comprehensive theoretical and experimental study by Radian (Lowell, 1970) involves 41 neutral and ionic species in solution and 7 solid components (Karlsson, 1980).

4. Dual Alkali Scrubbing

The dual alkali process involves two steps: first, SO₂ present in flue gas is absorbed in an alkaline sodium solution to form primarily sodium sulfite. In the regenerative reaction, limestone is added to the reactor. The products formed are calcium-sulfur salts which are disposed as a moist cake. The reactions are summarized below (Valencia, 1982):



This process is an alternative to sodium single-alkali throwaway processes where costly chemicals are not regenerated.

5. Dry Sorbent FGD

Dry sorbent FGD processes involve injection of a sorbent in powder form or water-based slurry into the flue gas stream. In powder form, the sorbent is injected into a flue gas duct upstream of a fabric filter. In the slurry type, hereafter referred to as dry FGD, solution is atomized to small droplets of 70-200 μm diameter by a disk or nozzle atomizer and sprayed into the flue gas bearing SO_2 . The flue gas is adiabatically humidified and the slurry is evaporated to form an apparent dry product. For FGD applications the sorbent is often calcium-based slurry or a sodium solution which is contacted with flue gas containing SO_2 during and following the drying process (Kelly, 1980). The chemical reactions in this process are similar, even though more involved due to simultaneous drying, to reactions in wet scrubbers. Also the presence of CO_2 in the flue gas complicates the process. According to Getler (1979) the reactions occur in several steps in the spray dryer and can be described as follows:

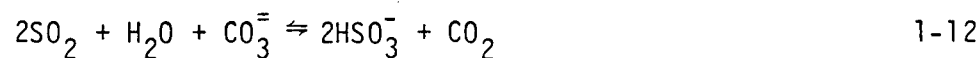
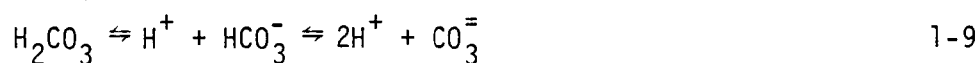
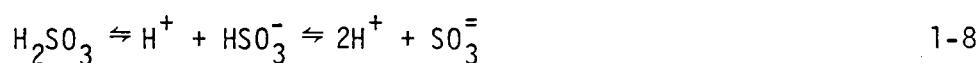
1. Diffusion of SO_2 and CO_2 through liquid film of the atomized $\text{Ca}(\text{OH})_2$ droplet



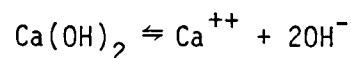
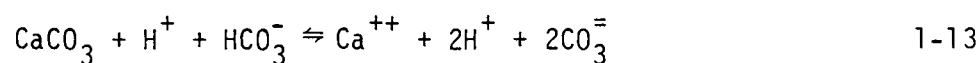
2. Dissolution of SO_2 and CO_2



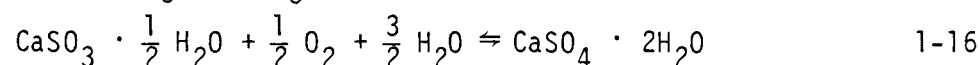
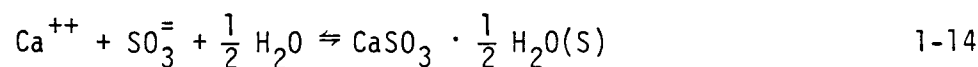
3. Dissociation in alkaline medium



4. Dissolution of solids



5. Formation of salts



Since the above reactions require an aqueous medium, the amount of water present in the slurry and spray-dried solids is an important factor. From the above reactions it can be seen that both SO_2 and CO_2 react with the available lime. The partial pressure of CO_2 in the flue gas is at least 100 times that of SO_2 but due to rapid hydration and oxidation of SO_2 in solution SO_2 has higher transfer rates than CO_2 . The mass transfer coefficients for the spray drying process is not known but liquid phase mass transfer coefficients (air-water interface) for SO_2 and CO_2 are 34420 cm/hr and 20 cm/hr, respectively (Thibodeaux, 1979).

The rate of moisture loss by the products is controlled by the approach-to-saturation temperature at the outlet of the spray dryer. The smaller the approach-to-saturation, the larger the evaporation period of products resulting in higher SO_2 removal efficiencies. It is reported that a 10°F reduction in the temperature at the outlet of the spray dryer (from 30°F approach to a 20°F approach), would cause an increase of 10 percent in SO_2 removal efficiencies (Hurst, 1981). An approach-to-saturation of less than 20°F results in maintenance problems in both the spray dryer and the fabric filter, however. The residence time of the flue gas in the spray dryer also affects the drying. The slower the drying rate and the longer the drying time of the droplet, the more reaction that can theoretically occur.

The major driving force behind the commitment of the utility industry to dry scrubbers, i.e., approximately 4000 MW, or 6.5 percent

of the total generating capacity (Ireland, 1982), is the potential for reducing both capital and operating costs relative to conventional wet limestone systems. An inherent advantage of the dry FGD system is production of a dry solid waste product that eliminates sludge handling equipment of wet systems. It should be noted, however, that products from sodium-based dry FGD systems are quite water soluble, thus leading to leachability problems. Other advantages of dry FGD include energy savings and lower maintenance requirements since thickeners, centrifuges, vacuum filters and mixers used in handling wet sludge waste products from wet systems are eliminated (Ireland, 1982).

Reagents used in dry FGD systems are much more costly than limestone and a higher stoichiometric ratio of sorbent to entering SO_2 is sometimes required. Therefore, wet limestone scrubbing systems are favored as far as reagent utilization and sorbent-related operating costs are concerned. To improve the utilization, other additives can be added which improve reaction conditions in the spray dryer. Another alternative is to recycle waste products. Waste products can be recycled from the spray dryer, particulate collector, or both.

That solids recycle is beneficial with regard to increased SO_2 removal efficiencies is known. However, the mechanisms that are responsible for the observed increase in SO_2 removal efficiency are not certain. According to Gude (1979) several features of products contribute to the observed benefit: recycled material has some

unreacted lime, fly ash in the product has available alkalinity, and product provides a surface on which fresh lime particles can agglomerate. Bench-scale studies conducted by Davis et al. (1981) have shown that solid Ca(OH)_2 adsorbs gaseous SO_2 . Sorption studies by Stern (1978) indicated that sodium-based additives as well as calcium-based sorbents show characteristic adsorption curves. Getler (1979) has shown the presence of unreacted calcium in the core of waste particles. Getler's results suggest that ball milling of the solids would expose the unreacted lime but limited tests conducted by Stevens (1980) have shown little benefits of this concept. Similar tests conducted at The University of Tennessee dry FGD pilot plant confirm the benefit of milling but do not attribute it to exposure of unreacted lime because analyses of products show negligible amounts of unreacted lime present. One factor in this apparent inconsistency is the product size. Larger products may have a core of lime which remained unreacted because of the limited penetration of SO_2 .

C. PRINCIPLES OF ADSORPTION

1. Types of Adsorption

Adsorption processes take advantage of the ability of certain solids to separate gaseous or liquid components preferentially from a flue stream. This phenomena involves atoms of surface molecules which have no like atoms above the plane with which to form a chemical bond. This unbalance is overcome by an inward attraction of an adsorbate molecule (gaseous or liquid) onto the solid surface (Levenspiel, 1967).

According to Weber (1972), adsorption is a surface phenomenon that is possibly due to either electrical forces or Van der Waals' attraction or chemical reaction. For the first type, presence of a charged site on the surface of the adsorbent attracts ions of the adsorbate. In physical adsorption, intermolecular forces are responsible for concentrating one substance on the surface of another. In chemical adsorption, adsorbate and adsorbent molecules chemically react. Since an actual chemical reaction takes place in this type of adsorption, an increase in temperature has beneficial effects on the rate of adsorption whereas for physical adsorption the effect is negative. Another feature of this type which is different from physical adsorption is that no movement of molecules is possible within the interface or on the surface.

Since adsorption is a surface phenomenon the rate of adsorption is directly proportional to specific surface area, defined as the portion of total surface area available for adsorption. Thus, the more finely divided and the more porous the solid is, the higher the adsorption capacity would be. It should be noted, however, that surface area is not the only factor having influence in adsorption processes; the solubility of solute, the surface character of adsorbent, the pH of a solution from which adsorption occurs, and prevailing temperature are some other contributing factors.

2. Adsorption Isotherms

At equilibrium in an adsorption system there is a defined distribution of adsorbate to adsorbent ratio. This ratio, q_e , is a

function of several parameters including the concentration of the solute and nature of solution. It is defined as the amount of adsorbate adsorbed per unit weight of adsorbent. A plot of this parameter versus the concentration of solute at equilibrium, C , is called an adsorption isotherm. In Figure I-1 curves A and B show the relationship between q_e and concentration at equilibrium for favorable and unfavorable adsorption processes. For favorable adsorption processes adsorbate is adsorbed even at low concentrations whereas for unfavorable processes only at close to saturation concentrations does an appreciable amount of adsorption take place. It should be noted that since adsorption processes are usually used for removing low concentration pollutants, terms like favorable and unfavorable are of importance. But for the processes which operate at saturation concentration all the time, unfavorable and favorable adsorption may not be different if unfavorable adsorbent peaks to high q_e levels at saturation concentrations.

Several types of models have been proposed to describe isothermal adsorption relations. The Langmuir adsorption model assumes deposition of solute on the surface of solid adsorbent in an apparent single layer in addition to constant and uniform energies of adsorption and no transmigration of adsorbate in the plane of the surface. The Brunauer, Emmett, and Teller (BET) model considers isotherms of multilayer adsorbate deposition. A given layer need not be completed before initiation of another. Another model is called the Freundlich model and it has been used for many years. This model

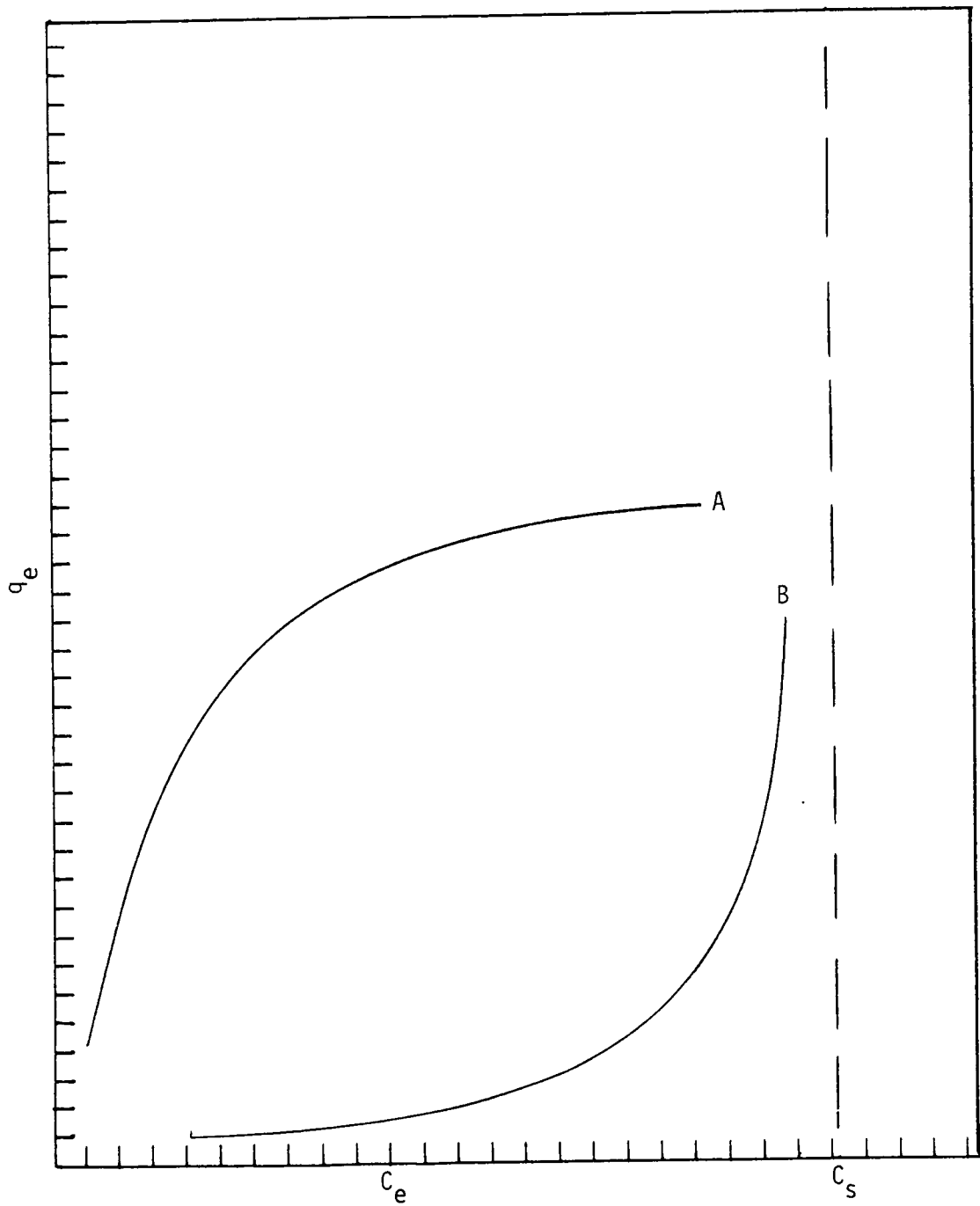


Figure I-1. Types of adsorption processes.

is a special case for heterogeneous surface energies in which the constant term related to net enthalpy in the Langmuir model varies as a function of adsorbate-adsorbent ratio, q_e , because of variation in heat of adsorption (Adamson, 1967). It generally agrees with experimental data over moderate ranges of concentration. Linear forms of the above models are as follows (Weber, 1972):

$$\frac{1}{q_e} = \frac{1}{Q^\circ} + \left(\frac{1}{bQ^\circ}\right)\left(\frac{1}{C}\right) \quad \text{Langmuir} \quad (6)$$

$$\frac{C}{(C_s - C)q_e} = \frac{1}{BQ^\circ} + \left(\frac{B - 1}{BQ^\circ}\right)\left(\frac{C}{C_s}\right) \quad \text{B.E.T.} \quad (7)$$

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C \quad \text{Freundlich} \quad (8)$$

where

q_e = amount adsorbate per unit weight of adsorbent;

C = concentration of adsorbate at equilibrium;

C_s = saturation concentration of adsorbate;

Q° = number of moles of adsorbate per unit weight of adsorbent
in forming a complete monolayer;

B = constant of energy of interaction;

b = constant related to net enthalpy, ΔH , of adsorption;

n = constant greater than 1;

K_F = constant, proportional to $RTnbe^{\Delta H/RT}$.

3. Breakthrough Curve

In operations involving stationary or fluidized-bed contacters, adsorbate flows through a column of adsorbent at a certain flow rate.

The solution containing adsorbate flows through regions of partially utilized adsorbent to areas of fresh material. In this way the full capacity of the adsorbent can be realized with time until exhaustion occurs or the concentration of adsorbate becomes too high to be unacceptable. In the initial stages of operation the adsorbate is adsorbed most rapidly by the immediate layers in the direction of flow. The amount which escapes these layers is removed by the next adjacent layers. With time the whole column becomes saturated with adsorbate and no detectable decrease in adsorbate concentration is observed.

The breakthrough curve is a plot of concentration at any time over initial concentration of solute, C/C_0 , versus time or volume of solution treated, T or V , respectively (Weber, 1972). For most adsorption processes breakthrough curves with a characteristic S shape are observed, with different slopes and breakthrough points. Among other factors, the depth of the adsorption column and the velocity of flow determine this shape. For an infinite rate of adsorption the breakthrough curve would be vertical. Although a disadvantage from a control standpoint, it is advantageous in that the entire bed would be saturated, the overall effect being the removal of more pollutant for a given size of bed. The other extreme is that of a flat breakthrough curve. In this situation much of the bed would not be saturated at the time of breakthrough. Thus longer beds would be required to keep the length of operation reasonable. This leads to other disadvantages such as a higher pressure drop across the bed.

An ideal breakthrough curve is shown in Figure I-2. The primary adsorption zone in fixed bed reactors is defined as the region over which the influent concentration is reduced from C_x to C_b . It is assumed that this zone has a constant length throughout the operation. The shaded area represents the amount of adsorbate adsorbed from the breakpoint to exhaustion and is given by

$$M_S = \int_{\bar{V}_b}^{\bar{V}_x} (C_0 - C) d\bar{V}_e \quad 1-17$$

This is not the total capacity of adsorbent within the primary adsorption zone at the breakpoint. The total capacity is $(\bar{V}_x - \bar{V}_b)C_0$. Thus, the fractional ability of the adsorbent in the zone to adsorb solute is

$$f = \frac{M_S}{(\bar{V}_x - \bar{V}_b)C_0} \quad 1-18$$

If $f = 0$ (saturated adsorbent in the zone) the time of formation of zone should be essentially the same as the time required for the zone to travel a distance equal to its own height. If $f = 1$ (the zone free of adsorbate) the zone-formation time should be essentially zero (Treybal, 1980). The total amount of adsorbate adsorbed at the point of complete saturation per unit mass of adsorbent q_∞ , by a column of depth D and apparent packed density of ρ_p is given by (Weber, 1972)

$$S_S = \rho_p q_\infty D \quad 1-19$$

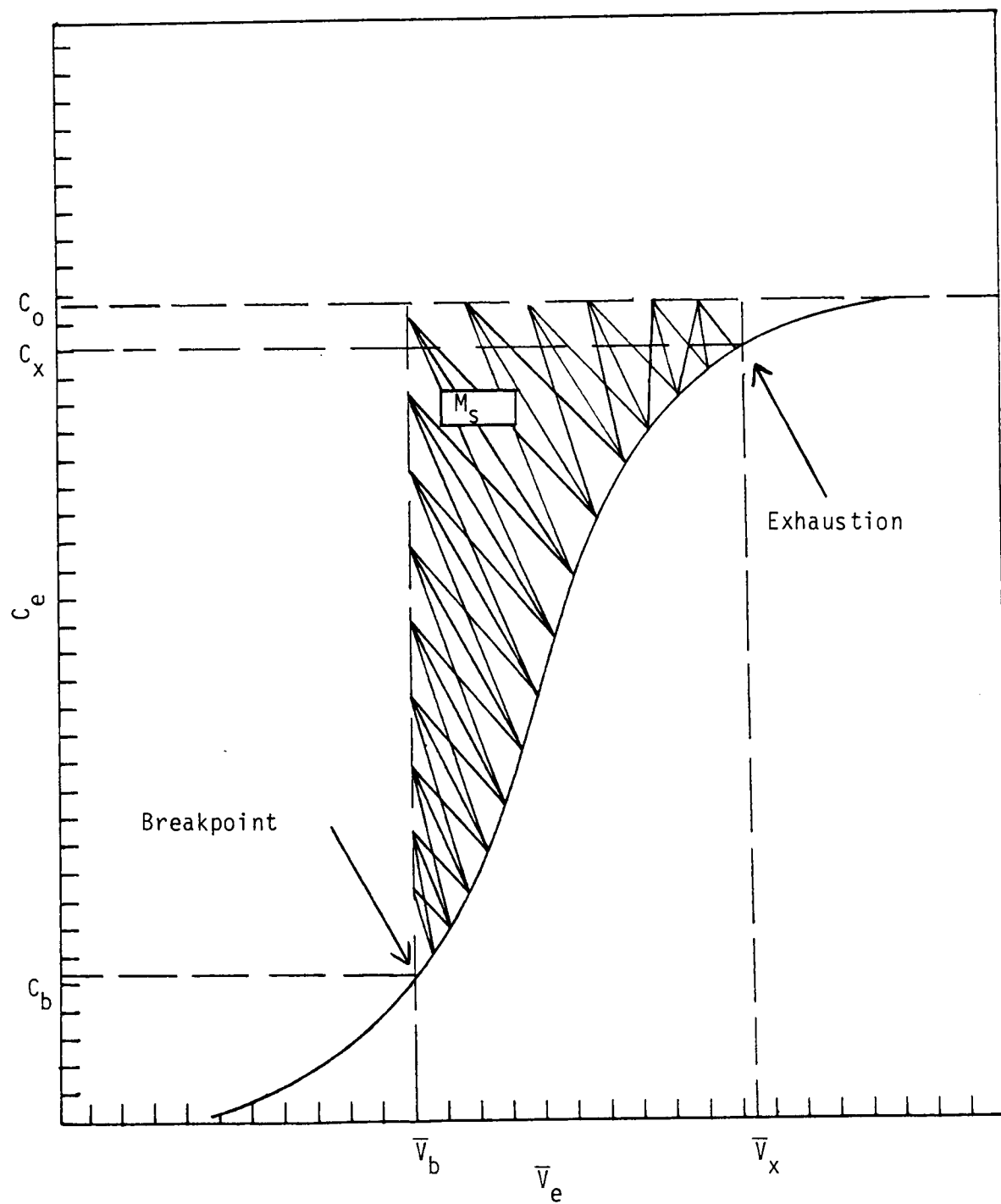


Figure I-2. Ideal breakthrough curve.

CHAPTER II

PURPOSE AND SCOPE

A. PURPOSE

This study was initiated to provide some insight into the possible explanations for the observed increases in SO_2 removal efficiency due to recycling of The University of Tennessee pilot plant Flue Gas Desulfurization (FGD) products. Analyses of dry scrubber FGD products showed that unreacted calcium hydroxide in products, if any, could not be totally responsible; the remainder being due to some other phenomenon. The observation that ball milling the products before injection resulted in further SO_2 removal enhancement, led to the thought that some surface phenomena may be responsible, specifically, adsorption, possibly followed by chemical reaction. It follows then that SO_2 in the flue gas can be absorbed by the slurry drop and react on the surface of $\text{Ca}(\text{OH})_2$ particles, with calcium ions in solution, and with calcium on the surface of the product.

B. SCOPE

This study was designed to investigate the potential for the accumulation of lime on a recycle product during the mixing prior to atomization. Typical concentrations of lime used in the process were such that the solution was saturated all the time and particulate

lime was present. It was hypothesized that upon addition of product a surface would be available onto which calcium ion could adsorb. The extent of this adsorption could depend on the prevailing conditions.

If calcium was adsorbed onto the surface or into the pores of the product particle, it would be practically separated from the aqueous phase. It was hypothesized that this may have allowed more calcium dissolution from Ca(OH)_2 particles, resulting in smaller Ca(OH)_2 particles. When slurry was fed into the spray dryer, SO_2 could react with calcium ions in solution, with calcium on the surface of product, and with Ca(OH)_2 particles. It was hypothesized that the increased "surface" lime produced in this fashion had an overall effect of making more lime available for fast reaction with SO_2 within the spray dryer residence time constraints.

The behavior of products with regard to Ca(OH)_2 adsorption bench-scale tests were studied. Particle-free saturated solution of Ca(OH)_2 was contacted with products generated at different stoichiometric conditions and/or with different surface areas. Adsorption columns and equilibrium conditions were set up to generate data for construction of breakthrough curves and adsorption isotherms. To obtain further insight into the chemical composition of products, tests were also conducted to find CaCO_3 content of products generated at different conditions.

CHAPTER III

MATERIALS AND METHODS

A. PILOT PLANT FACILITY

The University of Tennessee dry flue gas desulfurization (FGD) pilot plant is a nominal 1000 ACFM facility located adjacent to the UT steam plant. It is a spray dryer/fabric filter combination using quick pebble lime as the sorbent. A schematic of the plant is shown in Figure III-1.

The flue gas was extracted from stoker-fired boilers via a suction fan located downstream of the pilot plant facility. The SO_2 concentration upstream of the spray dryer was controlled by injection of gaseous SO_2 from liquid SO_2 cylinders. A dilution air adjustable inlet was used to control the temperature of the flue gas upstream of the spray dryer.

The spray dryer was seven feet in diameter and housed a Stork-Bowen rotating disk atomizer capable of speeds of 11,000 to 19,000 rpm. The baghouse consisted of 4 fiberglass filter bags, each of which were 32 feet long and 11.5 inches in diameter (air/cloth ratio = $2.6/1 \text{ CFM/ft}^2$). The fabric filter collector was equipped with a low-energy shaker for cleaning purposes.

Flue gas extracted from the boiler entered the spray dryer concentrically around the atomizer. A set of vanes around the atomizer imparted an angular downward motion of flue gas. This

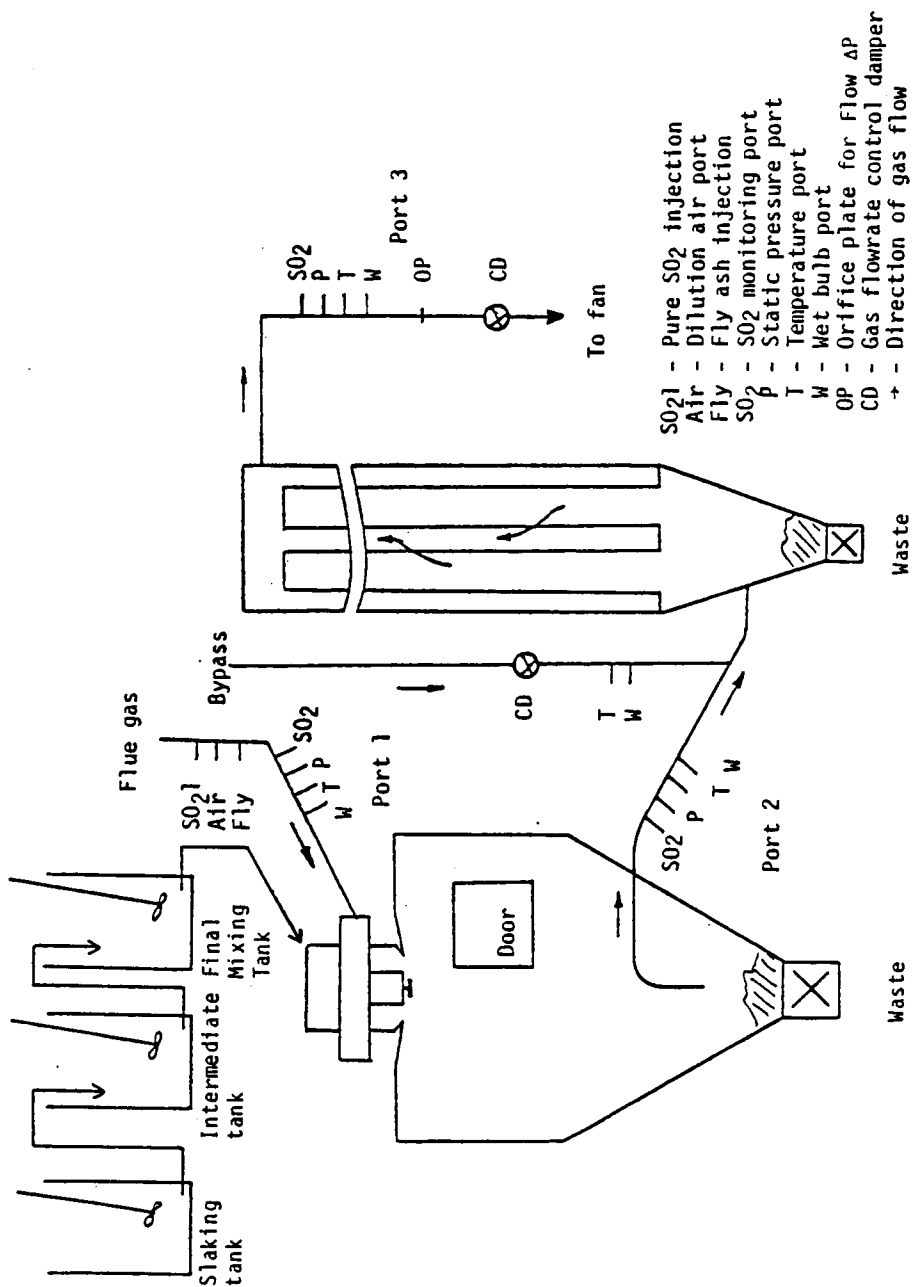


Figure III-1. Schematic of FGD pilot plant.

provided an optimum condition for mixing and reacting of water-based lime slurry with flue gas. The product-laden flue gas then entered the baghouse via a cross-over duct. Product and fly ash was collected on the bottom of the spray dryer and on the fabric filters. Rotary valves located on the hoppers of the spray dryer and baghouse were used to remove the solids.

Calcium hydroxide slurry was prepared by slaking of quicklime at a 3.5/1 mass ratio of water to lime, followed by dilution to the appropriate concentration. Titration with 3N HCl was used to measure the available hydroxide alkalinity from which the lime concentration was extrapolated. To accomplish recycle tests a predetermined mass of product was added to the lime slurry in such a way that a 4/1 mass ratio of product to lime was produced. For ballmill testing product was ballmilled in water before addition to lime. A mixing period of greater than thirty minutes was provided before injection to the atomizer. In this investigation, experiments were conducted to simulate the conditions of this part of the pilot plant facility. Products added here were hypothesized to make more "surface" lime available by adsorbing calcium ions. The slurry was injected into the spray dryer in small droplets produced by a spinning disk atomizer. The SO_2 concentrations at different ports (inlets and outlets) were monitored by a Lear Siegler SM800 SO_2/NO analyzer. Moisture content was measured using the wet-bulb method. Parameters of a typical test were as follows:

1. Inlet temperature range ($300 \pm 10^\circ\text{F}$).

2. Inlet SO_2 concentration (1000-1200 ppm).
3. Flue gas volumetric flow rate (1000 acfm).
4. Lime slurry preparation temperature (200-210°F).
5. Slurry concentration (0.3-0.8 lb CaO /gallon H_2O).
6. Temperature at the spray dryer outlet (18°F above the dew point).
7. Atomizer disc speed (17,000 rpm, equivalent to 75-85 micrometer mean drop diameter).

B. BENCH-SCALE EXPERIMENTS

1. Adsorption Column

A saturated solution of calcium hydroxide ($\text{Ca}(\text{OH})_2$) was passed through a 0.45 μm membrane filter to provide a particle-free solution. This $\text{Ca}(\text{OH})_2$ saturated solution ($1.6\text{-}1.7 \frac{\text{g Ca}(\text{OH})_2}{\text{liter}}$) was pumped to a cylindrical column whose height and diameter were 20 cm and 3 cm, respectively. The column contained 10-15 g of spray dryer product and glass wool was used at the inlet and outlet to trap the solids inside the column. Samples of solution were taken with time for 20-25 minutes and concentrations were measured titrimetrically using 0.15-0.25 N HCl. Both phenolphthalein and methyl orange endpoints were recorded to have a measure of carbon dioxide absorption even though such possibility was eliminated by sealing the system from the atmosphere.

2. Complete Mix Reactions

A saturated, particle-free solution of Ca(OH)_2 was contacted with 0.10 to 40 grams of spray dryer products generated at different stoichiometric ratios to generate isotherm curves. To provide a complete mix regime of contact the flasks were placed in a Brunswick Scientific Shaker set at 200-250 rpm and were shaken for two hours which was established by trial and error to be enough time to reach equilibrium. The supernatant was passed through a $0.45\ \mu\text{m}$ membrane filter and concentrations were titrimetrically measured. The flasks were sealed from the atmosphere throughout the experiment.

For total capacity determinations, 10 grams of five different stoichiometric ratio products were contacted with nine 300-ml-solutions of Ca(OH)_2 . Products were placed in the flasks, 300 ml saturated solutions of Ca(OH)_2 were added, reaction flasks were sealed from atmosphere, and were shaken for 3 to 4 hours. Solutions were vacuum filtered through a $0.45\ \mu\text{m}$ membrane filter and the concentration of a portion of it was measured. The rest of the supernatant was then discarded and new saturated solutions were added, flasks were sealed from atmosphere, and were shaken for 3-4 hours. This procedure was repeated nine times. For the last one there was no measurable Ca(OH)_2 pick-up by products, an indication of exhaustion of capacity. The difference in initial and final concentrations for each set was added to get total capacity. Again, double-endpoint titrations were conducted to prevent any misleading interpretations.

3. Carbonate Analysis

Spray dryer products generated at different stoichiometric ratios were also analyzed for calcium carbonate content. A closed-loop system was set up consisting of a reaction vessel, absorption flask, trap containers, and a pump as shown in Figure III-2. A known weight (0.3-0.5 gram) of spray dryer product was first contacted with 3 ml of 3 percent hydrogen peroxide to oxidize any sulfites present to sulfates. This oxidized sample was then introduced into the reaction vessel containing warm concentrated (6N) sulfuric acid. The reaction vessel was immediately sealed from the atmosphere to prevent escaping of any CO_2 generated. Carbon dioxide generated was passed through a condenser into a trap flask and then through an air diffuser to the absorption vessel containing a known volume of 0.1-0.15 N barium hydroxide solution where it partially reacted with barium hydroxide. The unreacted portion was circulated through the system many times to provide enough time for reaction of all CO_2 with barium hydroxide. The absorption flask was removed from the system and titrimetrically analyzed for barium hydroxide concentration. The difference between initial and final carbonate content was the amount contributed by product. Two such runs were conducted for each sample and the results were averaged.

C. OTHER ANALYSES

Other analyses conducted on spray dryer products included moisture content, surface area, and particle size determination. Moisture content was simply the difference between the initial weight

A. Reaction vessel containing 6N H_2SO_4

B. Water bath

C. Sample intake

D. Condenser

E and F. Moisture trap

G. Absorption vessel

H. Circulating pump

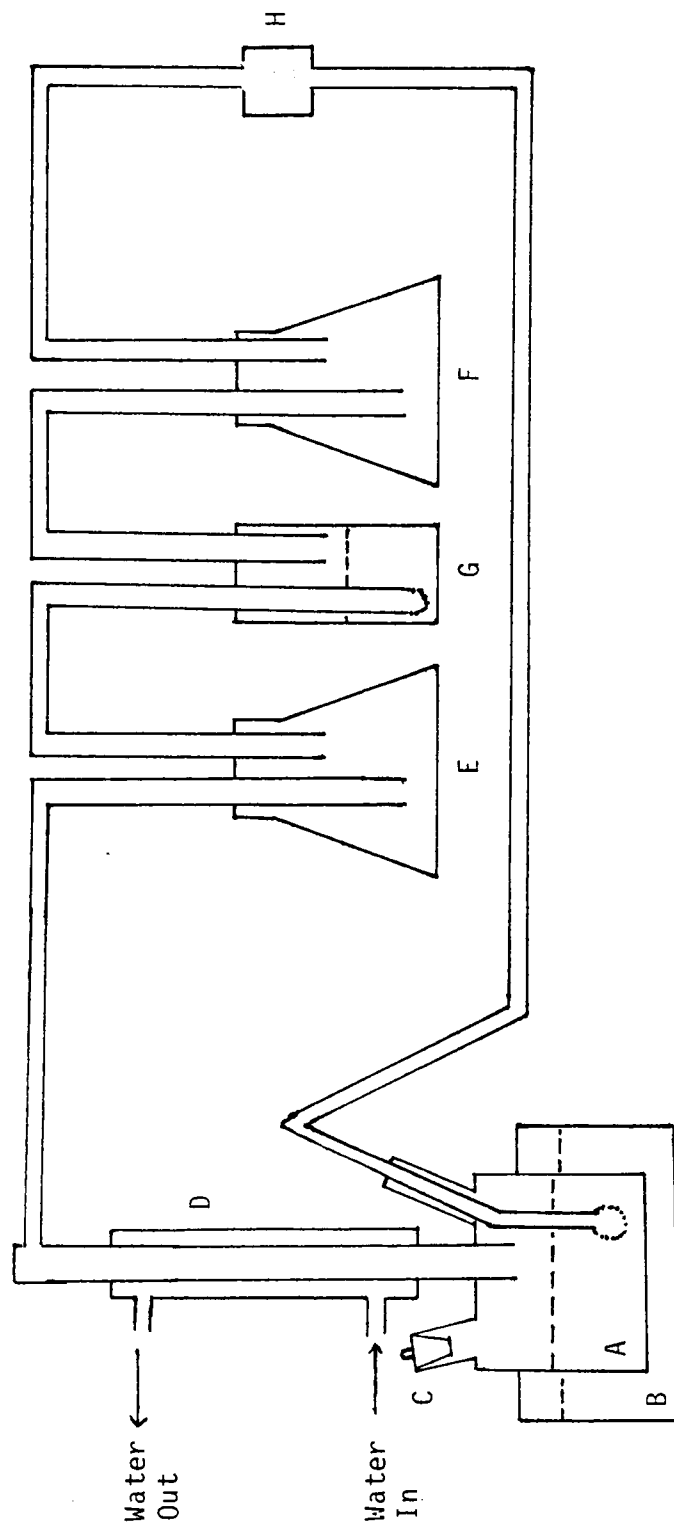


Figure III-2. Schematic of carbonate analysis apparatus.

of product before dessication and after it was dessicated. For surface area and particle size measurement, the instruments listed in Table III-1 were used.

Table III-1. Physical parameters measured on FGD products

Physical Property	Instrument
Particle size distribution	Coulter Counter Model TA11
Surface area	Micromeritics Surface Area Analyzer

CHAPTER IV

RESULTS AND DISCUSSION

A. ADSORPTION COLUMN CHARACTERISTICS

To determine the extent to which The University of Tennessee FGD products adsorb $\text{Ca}(\text{OH})_2$ and also the time required for complete exhaustion of adsorption capacity, a series of tests were conducted in which products in a column were contacted with saturated solutions of $\text{Ca}(\text{OH})_2$. A summary of the results for each of the experiments is listed in Tables A-1 through A-5 in Appendix A. Graphical representations of the results are shown in Figures IV-1 through IV-5. Table IV-1 lists conditions under which products were generated along with other physical and chemical properties of the products. In Figure IV-6 total column capacities for individual products are shown. A list of equations used for calculations is provided in Appendix B.

One common characteristic of the experiments was the short breakthrough time due to a combination of factors such as amount of product used (10-15 grams) and flow rates (15-30 ml/min). Not enough product was available and lower flow rates could not be used because sampling time had to be extended beyond 30 seconds in order to collect enough solution for titration purposes. The breakthrough zone was not always adequately measured as can be seen in Figures IV-1 and IV-2. It is clear from the figures that total capacities were not high, calculated to be between one to eight mg $\text{Ca}(\text{OH})_2$ per gram

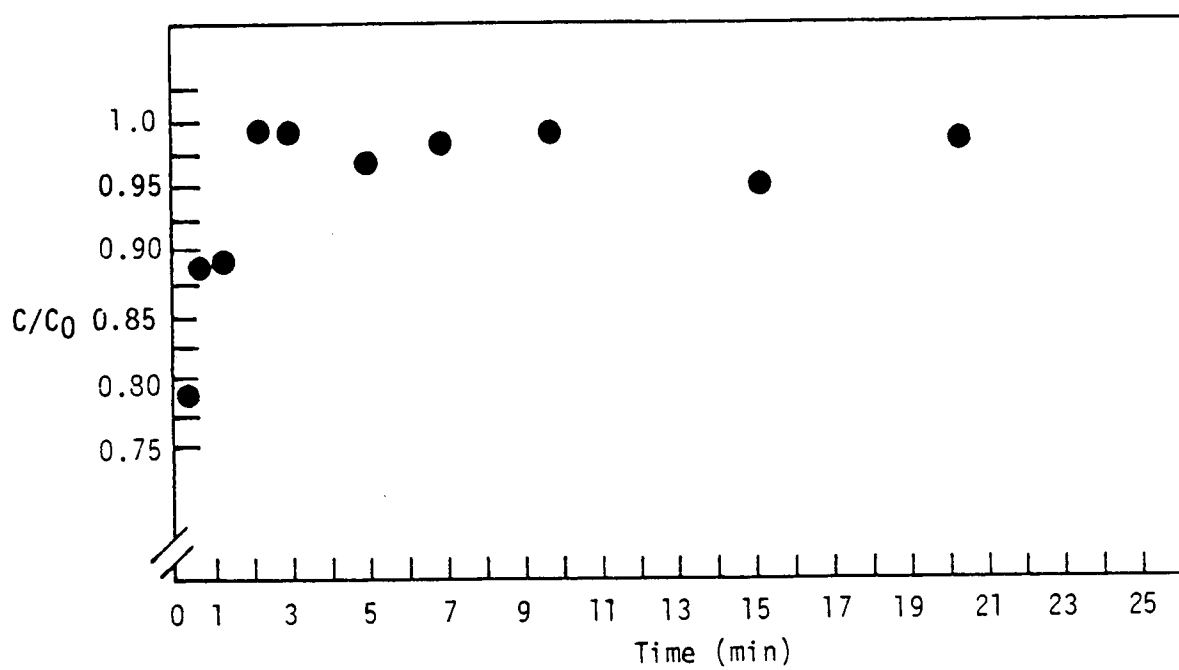


Figure IV-1. Breakthrough curve for spray dryer product generated at $SR = 1.56$.

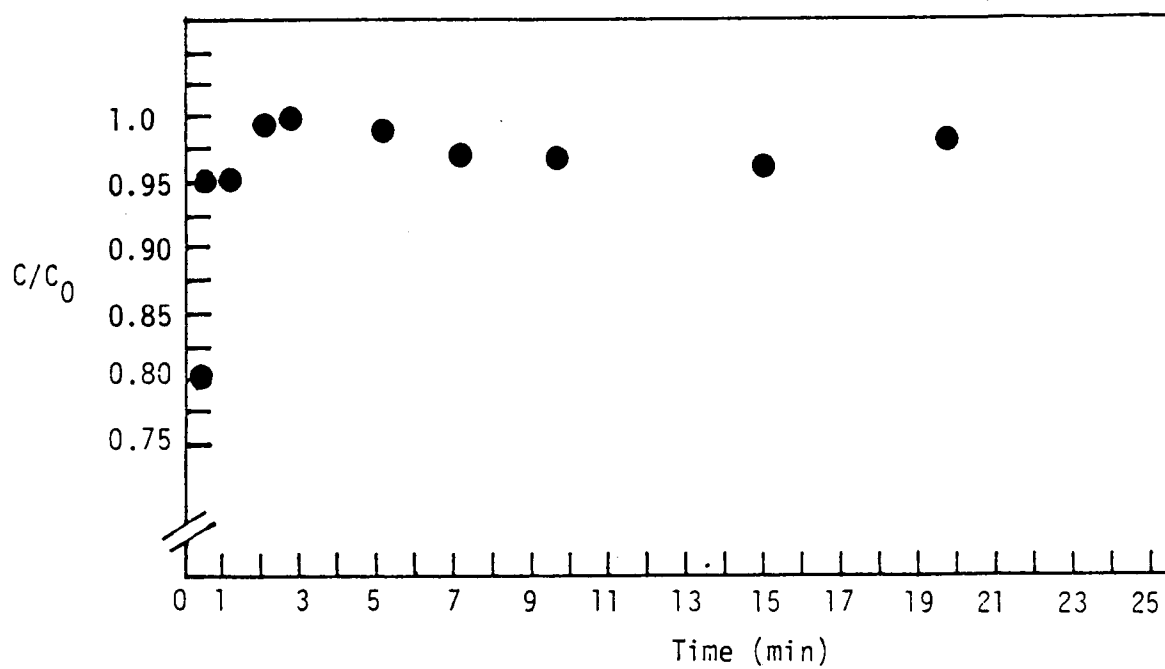


Figure IV-2. Breakthrough curve for spray dryer product generated at $SR = 1.7$.

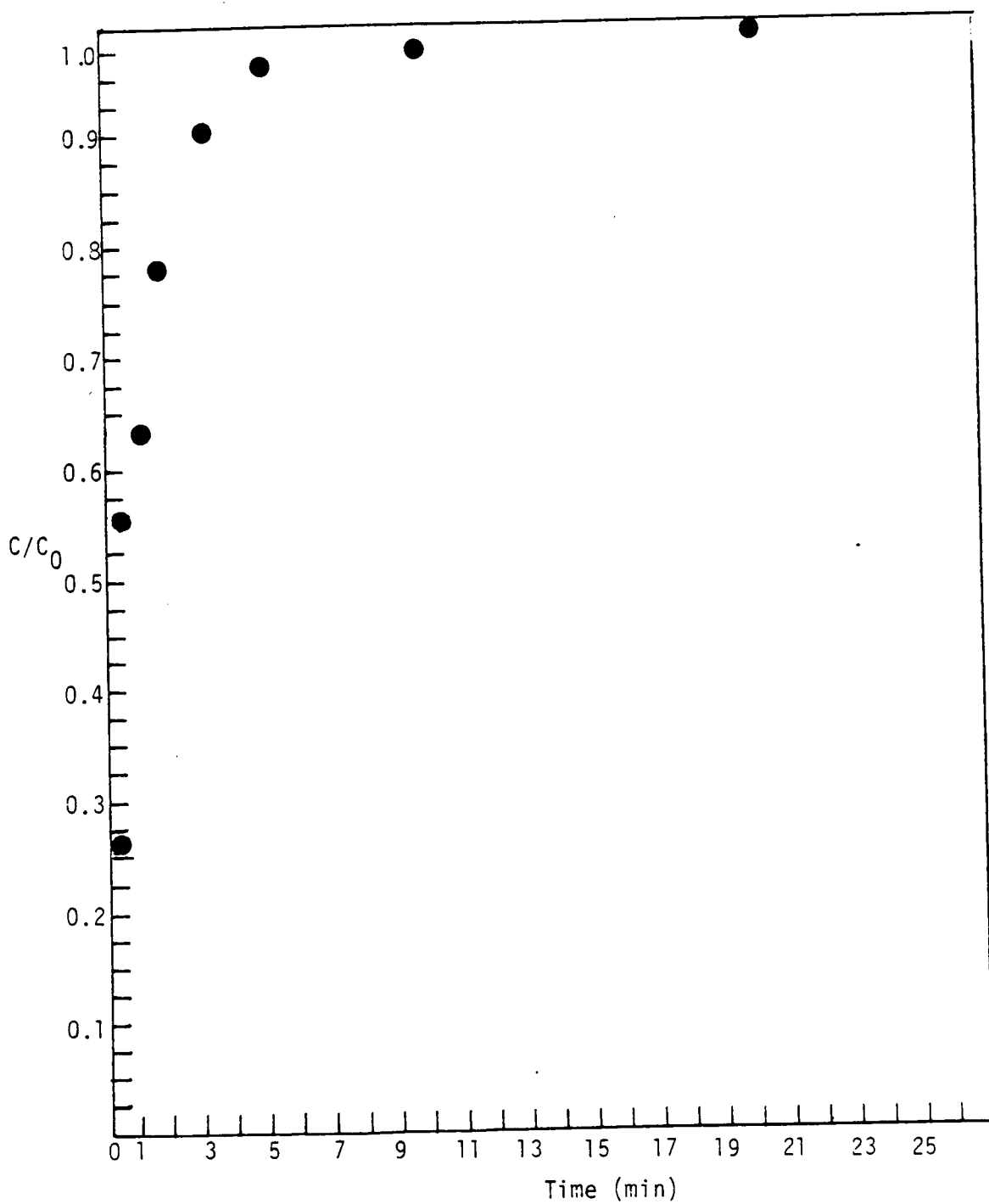


Figure IV-3. Breakthrough curve for spray dryer product generated at $SR = 1.22$.

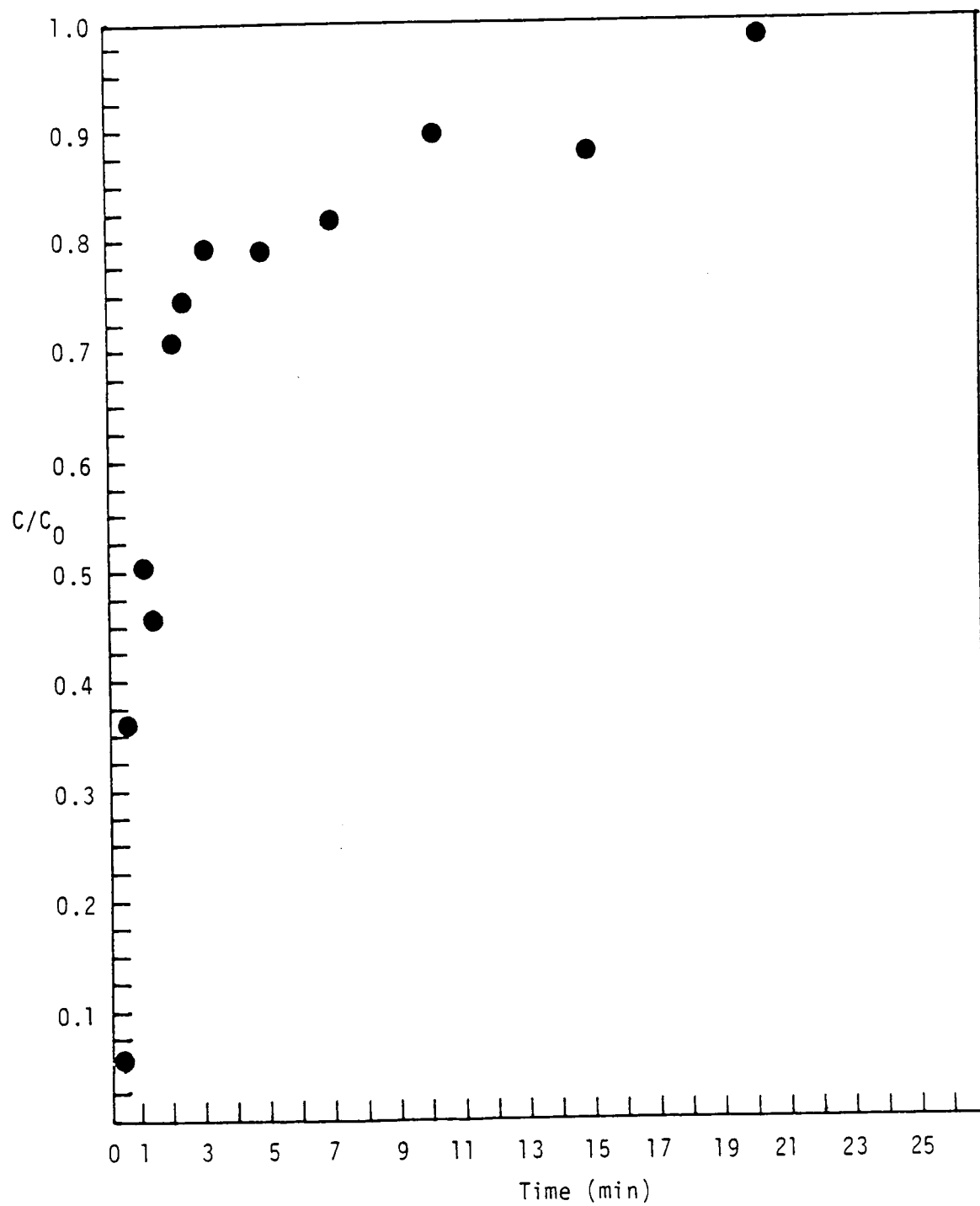


Figure IV-4. Breakthrough curve for spray dryer product generated at SR = 0.925.

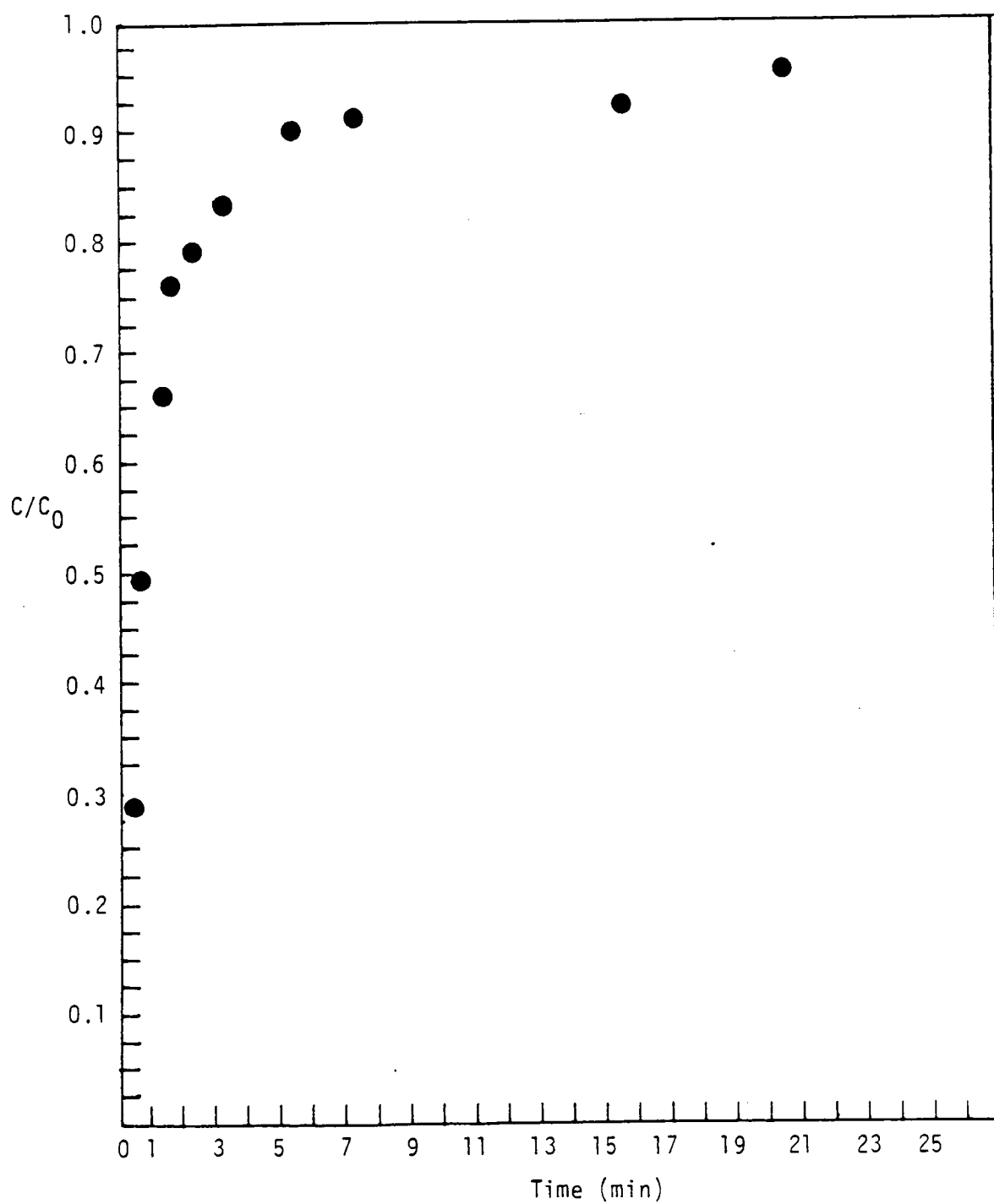


Figure IV-5. Breakthrough curve for spray dryer product generated at $SR = 0.695$.

Table IV-1. Properties of spray dryer products used in different experiments

Product Identification Number	Stoichiometric ^a Ratio	Spray Dryer Efficiency	Surface Area m ² /g Product	Percent Experimental CaCO ₃	Percent Moisture Content	Complete Mix Total Capacity mg Ca(OH) ₂ g Product	Column Total Capacity mg Ca(OH) ₂ g Product
3	1.56	0.821	20.95	22.1	5	9.5	1.66
5	1.70	0.858	11.87	60.2	2	7.1	1.82
18	1.22	0.793	21.39	36.0	9	14.0	4.90
28	0.925	0.690	15.61	20.6	4	22.5	6.86

^a Stoichiometric ratio = $\frac{\text{mole CaO added}}{\text{mole SO}_2 \text{ added}}$

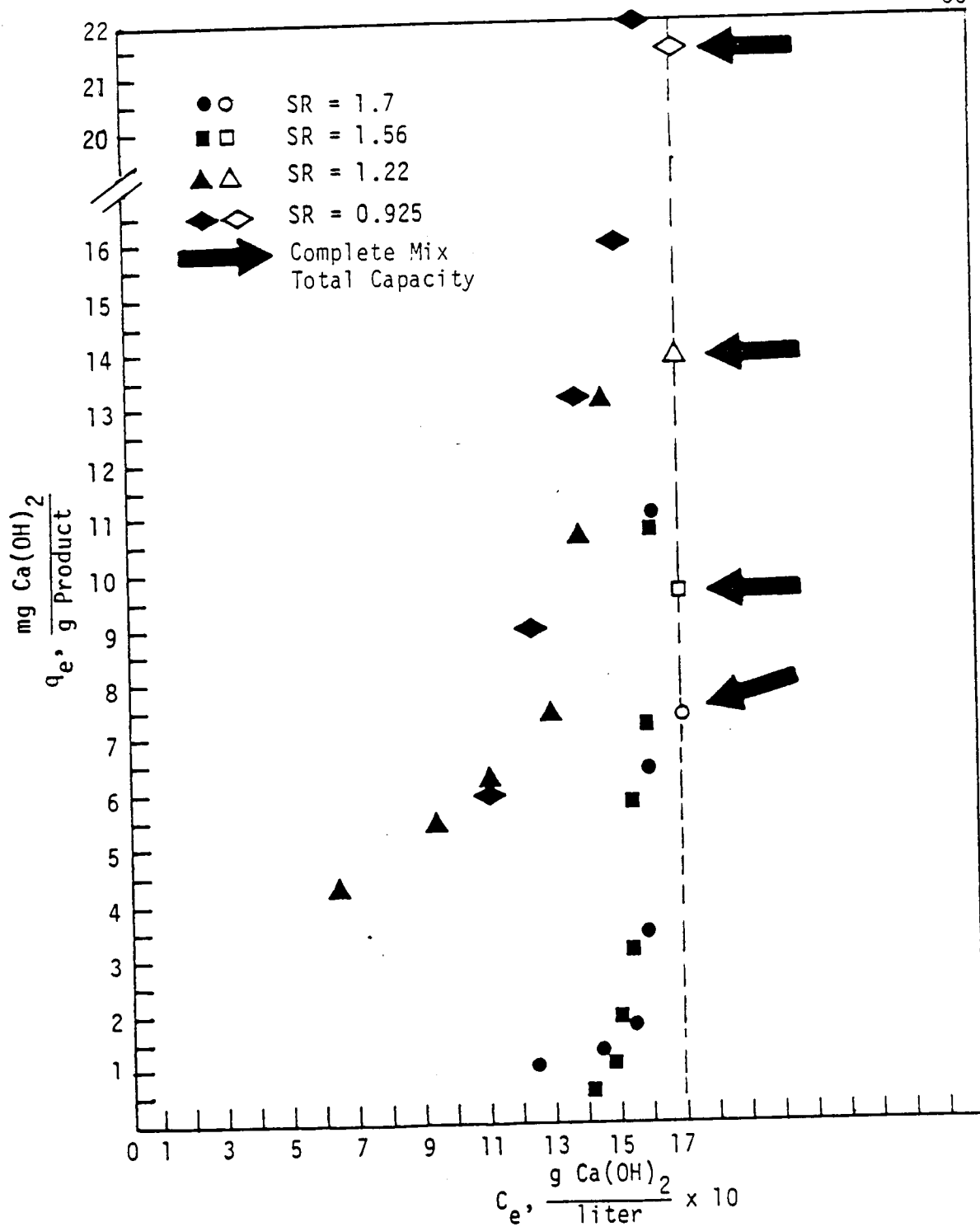


Figure IV-6. Isotherm curves of spray dryer products and their total capacity from adsorption column and complete mix reactors.

product. The uncertainties associated with the behavior of adsorbent at early stages of the experiments imply that real total capacities may have been higher.

During the course of testing, it was suspected that a portion of the surface area may not come in contact with $\text{Ca}(\text{OH})_2$ solution because of compaction. This condition would result in underestimation of total capacity of products. To see if such was the case, a fluidized condition was set up by using a longer column and introducing nitrogen gas and $\text{Ca}(\text{OH})_2$ simultaneously. Results of these tests showed that total capacity of fluidization was the same as stationary beds, implying that all of the material was being utilized.

B. CHARACTERISTICS OF EQUILIBRIUM EXPERIMENTS

In order to observe the behavior of FGD products in completely mixed conditions, a series of reactors were set up for contacting saturated solution of $\text{Ca}(\text{OH})_2$ and products. These experiments were conducted at constant room temperature. Enough time, as determined by some preliminary tests, was allowed for the system to reach equilibrium. Tables A-5 through A-10 (Appendix A) summarize the results of isotherm experiments; the same data are represented graphically in Figure IV-6. Calculation procedures are shown in Appendix B.

It is observed from Figure IV-6 that the adsorptive capacity of the products dramatically increase at near saturation concentrations. With the observed behavior at saturation concentration, a second set of tests were conducted to simulate a constant saturation concentration.

Saturated solutions of Ca(OH)_2 (1.65 g Ca(OH)_2 /liter) in contact with products were changed several times until no more Ca(OH)_2 was adsorbed by products. Total capacities obtained as such are termed "total capacities for complete mix conditions" and are shown in Figure IV-6.

It is seen that total capacities from complete mix conditions were much higher than those obtained from column experiments even though close to 100 percent saturation concentrations were prevailing for both cases. As mentioned earlier, the column total capacities obtained could be less than the actual capacity of products due to the uncertainties associated with the early stages of experiments. It can be observed from Figures IV-1 and IV-2 that only a portion of breakthrough curve is present. Another difference was residence time which was a total of 20 minutes for column tests and a total of close to 10 hours for complete mix conditions. The fact that there is poor correlation between total capacities and specific areas, shown in Figure IV-7, suggests that the surface characteristics of products may not have been the only factor responsible for observed adsorptions.

C. COMPARISON OF BENCH-SCALE AND PILOT PLANT DATA

Tests were conducted at The University of Tennessee FGD pilot plant using lime as an additive. Products were also mixed with lime and injected into the spray dryer to see the contribution due to this modification. The results of these tests, plotted in Figure IV-8, show the relation between SO_2 removal efficiencies and stoichiometric ratio for lime and the increase in efficiencies due to product recycle

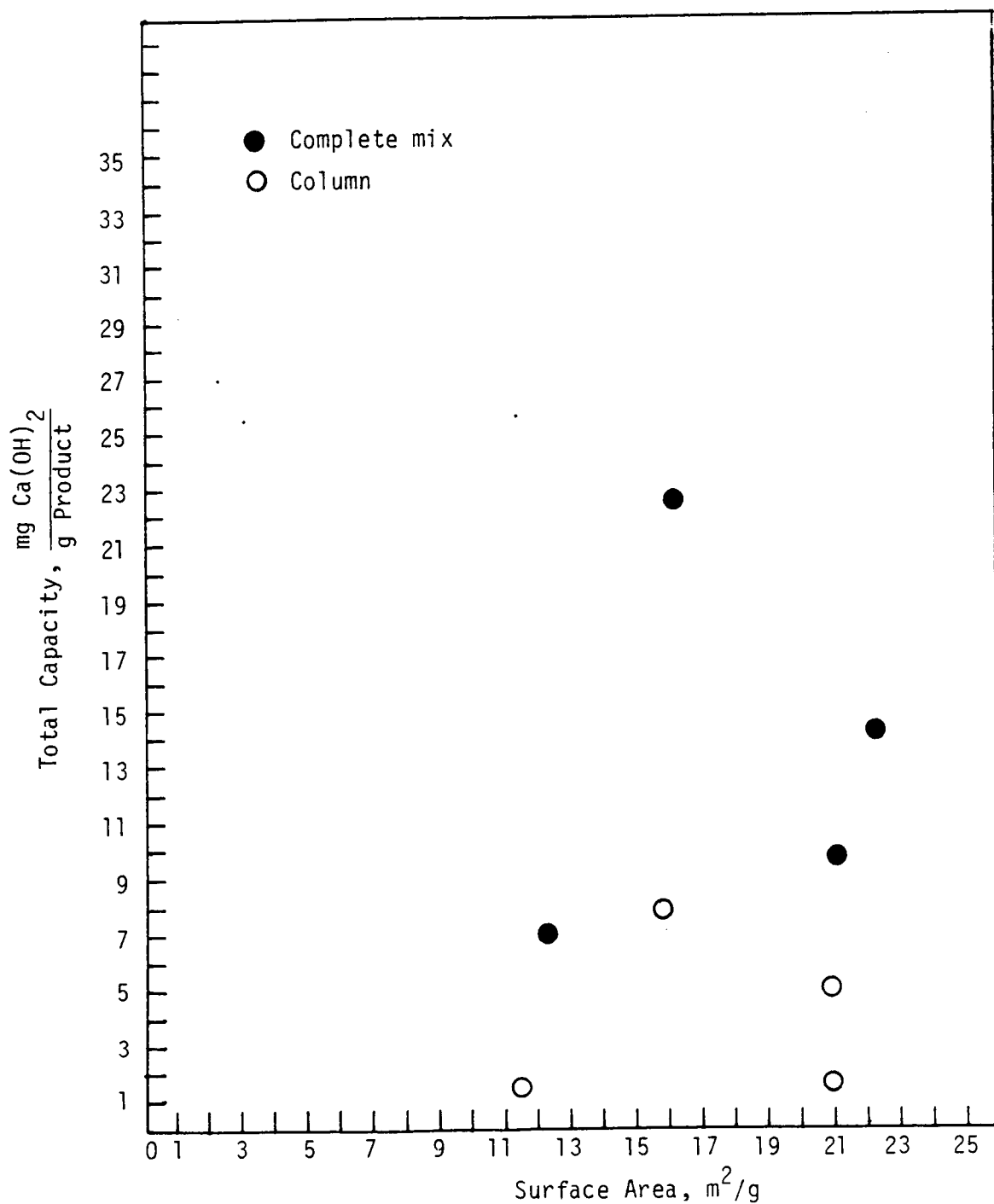


Figure IV-7. Complete mix reactor total adsorptive capacity of spray dryer products as a function of surface area of products.

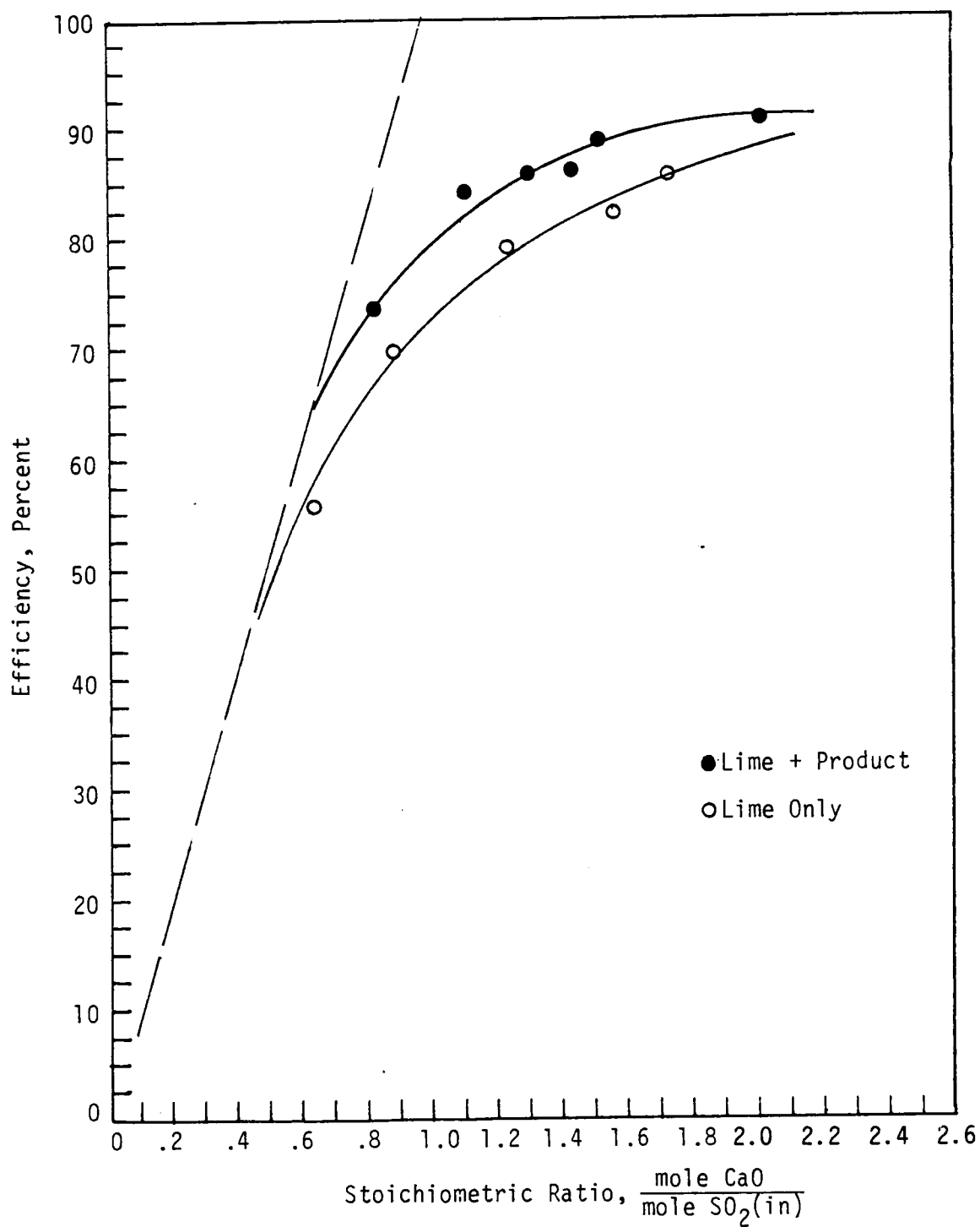


Figure IV-8. Pilot plant data showing the effect of product recycle.

at a mass ratio of 4/1 product to lime. The contribution of product recycle was calculated from Figure IV-8 by taking the difference in efficiency between the lime-only curve and the lime + product curve. This increase in efficiency was related to the increase in CaO utilization by assuming the theoretical relationship between efficiency and stoichiometric ratio, i.e., for SR of 1.0 there is 100 percent SO_2 removal. To illustrate the procedure, take the case at 1.7 SR. There was an increase in efficiency of 3.8 percent. This effect was due to addition of 381 g product ($56 \times 1.7 \times 4$) per 95.2 g CaO (56×1.7). The 3.8 percent efficiency corresponds to 0.038 SR or 2.1 g CaO. Thus, increase in CaO utilization per gram product was 5.6×10^{-3} g or 5.6 mg. This data along with information for other products are presented in Table IV-2.

Comparison of bench-scale adsorption data and pilot plant product recycle data indicated that adsorption could have been responsible for the observed increases in SO_2 removal efficiencies due to product recycle. The bench-scale adsorption capacities are higher than pilot plant increase in CaO availability by up to 21 percent. This 21 percent difference corresponds to only 1 percent efficiency. Considering the scatter of data around both product recycle and lime-only curves in Figure IV-8, 1 percent error in efficiencies is well justified. This is not to say that bench scale experiment analyses did not have any errors associated with them. As shown in Figure IV-8, at higher stoichiometric ratios, the effect of recycle decreases. Figure IV-9 shows that the CaCO_3 content of the products increase with increase in stoichiometric ratios, suggesting that part of the decrease in product

Table IV-2. Comparison of bench-scale equilibrium experiments and pilot plant data

Stoichiometric Ratio, $\frac{\text{mole CaO}}{\text{mole SO}_2(\text{in})}$	Increase in Efficiency Due to Recycle, %	Corresponding Increase in CaO Utilization g	Product Added, g	Unreacted Lime mg CaO/g Product	Pilot Plant $q_e, \frac{\text{mg CaO}}{\text{g Product}}$	Bench-Scale $q_e, \frac{\text{mg CaO}}{\text{g Product}}$	$\frac{\text{Experimental Actual}}{\text{Experimental}} \times 100$
1.7	3.8	2.1	381	0.70	5.6	7.1	21.1
1.56	5	2.8	349	0.65	8.0	9.5	15.8
1.22	6	3.36	273	0.68	12.3	14.0	12.1
0.925	8	4.47	207	0.42	21.6	22.5	4.0

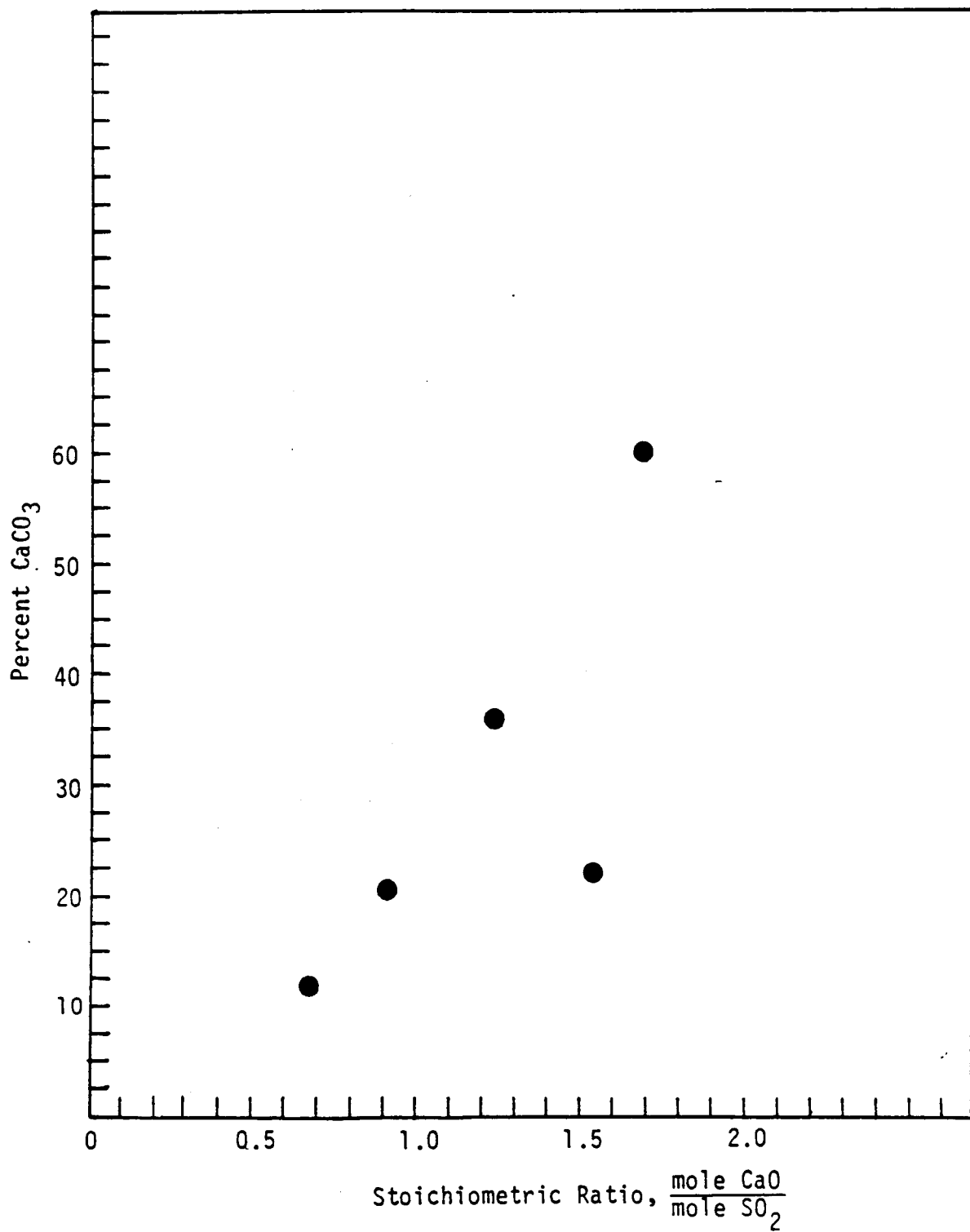


Figure IV-9. Calcium carbonate content of spray dryer products as a function of stoichiometric ratio.

recycle benefits may be due to the CaCO_3 content of products. This is supported by the fact that bench-scale adsorption capacities also decrease as the CaCO_3 content of products increase as shown in Figure IV-10. The results also show that bench-scale data agree with pilot plant data consistently. The results of tests conducted with pure CaCO_3 as shown in Figure IV-11 also suggest that CaCO_3 does not adsorb $\text{Ca}(\text{OH})_2$. It should be noted that pure CaCO_3 had a surface area of $1 \text{ m}^2/\text{g}$ whereas surface areas for products were in the range of $15\text{-}20 \text{ m}^2/\text{g}$. Pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, however, had a surface area of $5 \text{ m}^2/\text{g}$, but its adsorption capacities resemble that of products.

As mentioned earlier, efficiency curves in Figure IV-8 tend to converge at high stoichiometric ratio. Part of this could have been due to increase in the CaCO_3 content but some of it may as well have been due to short-circuiting in the spray dryer. If there was not enough residence time in the spray dryer, no matter how much lime was injected, no increase in SO_2 removal efficiencies would have been observed beyond a certain point. As shown in Table IV-2, as the stoichiometric ratio was increased, there was an increase in differences between pilot plant and bench-scale data. This would be expected if there is any short-circuiting since the effect of such a parameter would become more and more pronounced at higher stoichiometric ratios. This parameter can be checked by decreasing the flow to the system at constant lime slurry flow rate and observe efficiencies. In conducting such investigations, care should be taken to assure that other parameters such as drying time do not change. It would have been great to study the effect of CO_2 on the process, but since the

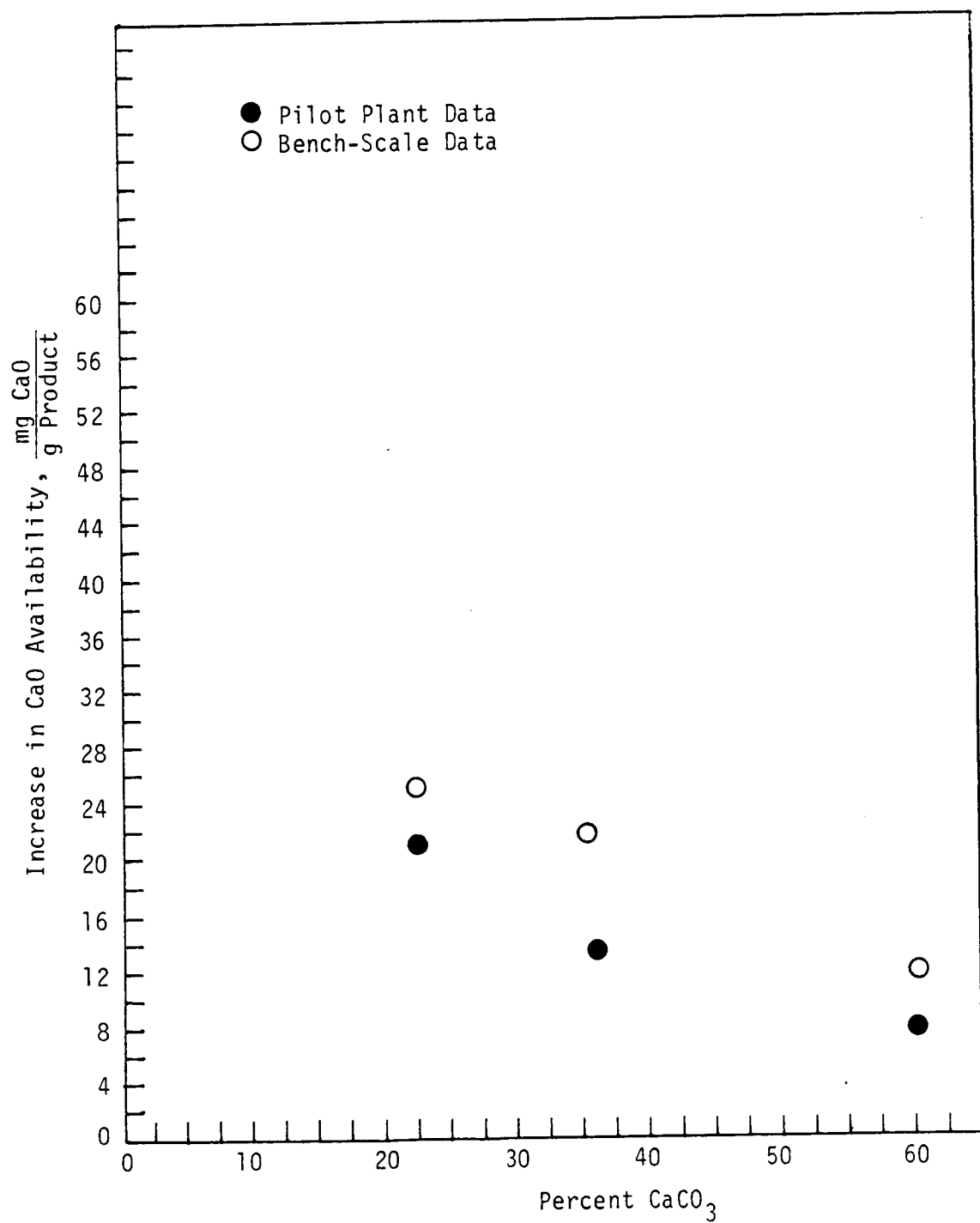


Figure IV-10. Increase in CaO availability as a function of percent CaCO_3 for bench-scale experiments and pilot plant data.

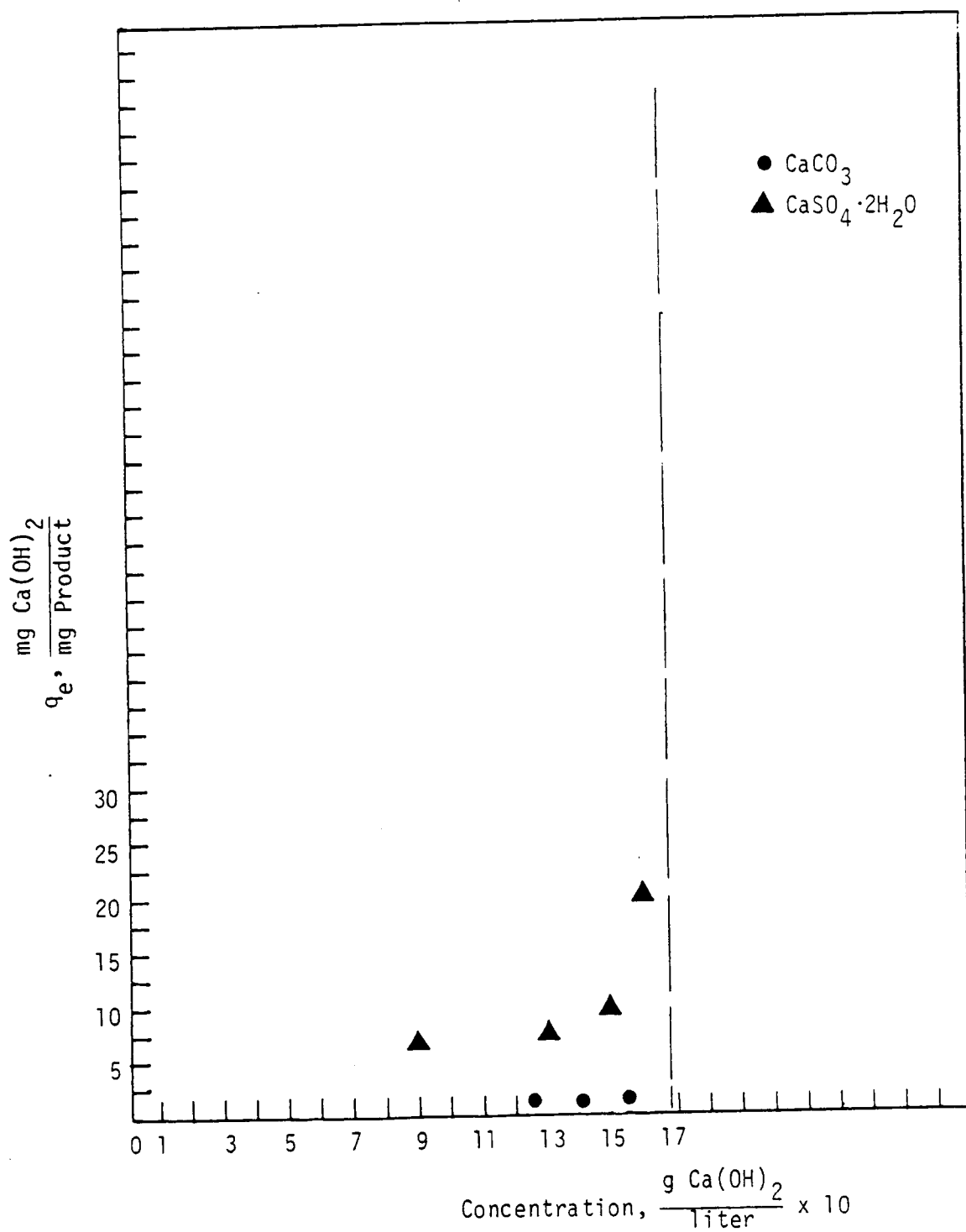


Figure IV-11. Adsorption isotherms of pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and pure CaCO_3 .

flue gas contains about 12 percent CO_2 by volume, the idea of setting conditions to discourage reactions of CO_2 with lime was not feasible.

CHAPTER V

CONCLUSION

The results of this investigation support the hypothesis that adsorption may be responsible for increases in SO_2 removal efficiencies as a result of product recycle. The role of CaCO_3 in products was shown to be negative with regards to adsorption thus decreasing the beneficial effects of recycle at high stoichiometric ratio. It is suggested, however, that CaCO_3 may not be the only factor responsible for the observed decrease in product recycle effects at high stoichiometric ratios; the possibility of short-circuiting is raised.

CHAPTER VI

RECOMMENDATIONS

The following suggestions for future work are made as a result of this investigation:

1. An investigation should be conducted to determine if there is any short-circuiting in the spray dryer. A preliminary study should be made to consider other parameters such as drying time associated with this investigation.
2. SO_2 removal efficiencies depend on the particle sizes generated by atomizers. In addition, the size of "particulate" lime in the slurry has an effect on penetration of SO_2 molecules. An investigation is needed to study the SO_2 removing capabilities of a range of particle sizes generated by different slaking conditions.

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APPENDIXES

APPENDIX A

ADSORPTION COLUMN AND EQUILIBRIUM DATA

The results of bench-scale tests for adsorption column and complete mix reactors are tabulated in the next several pages. Tables A-1 through A-5 contain information for adsorption column and Tables A-6 through A-10 present data for equilibrium experiments.

Table A-1. Adsorption column data for spray dryer product number three^a

Time (min)	Concentration of Ca(OH)_2 , g/liter	$\frac{\text{Final } \text{Ca(OH)}_2 \text{ Conc.}}{\text{Initial } \text{Ca(OH)}_2 \text{ Conc.}}$
0.25	1.348	0.799
0.75	1.50	0.889
1.25	1.507	0.893
2.25	1.739	1.03
3.25	1.725	1.02
5.25	1.630	0.966
7.25	1.652	0.979
10.25	1.665	0.987
15.25	1.603	0.950
20.25	1.665	0.987

^aConditions:

Stoichiometric ratio (SR) = 1.56

Spray dryer efficiency (EFF) = 0.821

Initial Ca(OH)_2 concentration, g/liter (C_0) = 1.687

Flow rate into column (Q), ml/min = 17

Table A-2. Adsorption column data for spray dryer product number five^a

Time (min)	C g/liter	C/C ₀
0.25	1.357	0.804
0.75	1.567	0.929
1.25	1.616	0.958
2.25	1.685	0.999
3.25	1.716	1.02
5.25	1.665	0.987
7.75	1.634	0.969
10.25	1.637	0.971
15.25	1.634	0.969
20.25	1.690	1.00

^aConditions:

SR = 1.70

EFF = 0.858

C₀ = 1.687 g Ca(OH)₂/liter

Q = 19.3 ml Ca(OH)₂/min

Table A-3. Adsorption column data for spray dryer product number eighteen^a

Time (min)	C g/liter	C/C ₀
0.167	0.261	0.163
0.75	0.416	0.259
1	0.879	0.548
1.5	0.999	0.622
2	1.23	0.768
2.5	1.37	0.852
3	1.46	0.910
3.5	1.48	0.924
5	1.55	0.965
8	1.57	0.976
10	1.59	0.988
15	1.60	0.997
30	1.603	0.999
48	1.601	0.998

^aConditions:

SR = 1.22

EFF = 0.793

C₀ = 1.605 g Ca(OH)₂/liter

Q = 16 ml Ca(OH)₂/min

Table A-4. Adsorption column data for spray dryer product number twenty-eight^a

Time (min)	$\overset{C}{\text{g Ca(OH)}_2/\text{liter}}$	C/C_0
0.25	0.108	0.064
0.75	0.380	0.361
1.25	0.851	0.504
1.75	0.783	0.464
2.25	1.186	0.703
2.75	1.259	0.746
3.75	1.331	0.789
5.25	1.333	0.790
7.25	1.395	0.827
10.25	1.494	0.886
15.25	1.471	0.872
20.25	1.673	0.992

^aConditions:

SR = 0.96

EFF = 0.687

$C_0 = 1.687 \text{ g Ca(OH)}_2/\text{liter}$

$Q = 15.67 \text{ ml Ca(OH)}_2/\text{min}$

Table A-5. Adsorption column data for spray dryer product number thirty-five^a

Time (min)	C g Ca(OH) ₂ /liter	C/C ₀
0.25	0.476	0.282
0.75	0.829	0.491
1.25	1.12	0.663
1.75	1.29	0.766
2.25	1.33	0.791
3.25	1.41	0.833
5.25	1.52	0.90
7.25	1.54	0.912
15.25	1.56	0.928
20.25	1.60	0.949

^aConditions:

SR = 0.69

EFF = 0.569

C₀ = 1.687 g Ca(OH)₂/liter

Q = 15 ml Ca(OH)₂/min

Table A-6. Equilibrium data for spray dryer product number five^a

Spray Dryer ^b Product wt., g	Final Concentration g/liter Ca(OH) ₂	mg Ca(OH) ₂ ^c g product
40	1.24	1.07
20	1.43	1.18
10	1.43	1.35
5	1.53	1.80
2	1.58	3.17
1	1.60	6.34
0.5	1.61	11.32

^aSR = 1.70; EFF = 0.858.^bNot corrected for moisture content.^cCorrected for moisture content.

Table A-7. Equilibrium data for spray dryer product number three^a

Spray Dryer ^b Product wt., g	Final Concentration g/liter Ca(OH)_2	mg Ca(OH)_2 ^c g product
40	1.42	0.64
20	1.46	1.05
10	1.49	1.87
5	1.52	3.03
2	1.55	5.83
1	1.60	6.99
0.5	1.61	10.7

^aSR = 1.56; EFF = 0.821.

^bNot corrected for moisture content.

^cCorrected for moisture content.

Table A-8. Equilibrium data for spray dryer product number eighteen^a

Spray Dryer ^b Product wt., g	Final Concentration g/liter Ca(OH) ₂	mg Ca(OH) ₂ ^c g product
50	0.66	4.4
30	0.95	5.3
20	1.11	6.1
10	1.33	7.3
5	1.42	10.7
3	1.48	13.3

^aSR = 1.22; EFF = 0.793.^bNot corrected for moisture content.^cCorrected for moisture content.

Table A-9. Equilibrium data for spray dryer product number twenty-eight^a

Spray Dryer ^b Product wt., g	Final Concentration g/liter Ca(OH) ₂	mg Ca(OH) ₂ ^c g product
40	0.29	3.6
20	0.71	5.1
10	1.11	6.0
5	1.25	9.0
2	1.43	13.3
1	1.53	16.1
0.5	1.58	23.1

^aSR = 0.925; EFF = 0.69.

^bNot corrected for moisture content.

^cCorrected for moisture content.

Table A-10. Equilibrium data for spray dryer product number thirty-five^a

Spray Dryer ^b Product wt., g	Final Concentration g/liter Ca(OH)_2	mg Ca(OH)_2 ^c g product
40	1.23	1.3
20	1.35	1.9
10	1.38	3.5
5	1.49	4.5
2	1.58	6.3
1	1.58	12.6
0.5	1.6	19.1

^aSR = 0.695; EFF = 0.560.

^bNot corrected for moisture content.

^cCorrected for moisture content.

APPENDIX B

DATA ANALYSIS

The next several pages are intended to explain the procedures used in calculations and analyses of data obtained during the course of investigation. Some of the self-explanatory procedures such as moisture content are omitted and attempt is made to provide details of each calculation in a straightforward fashion.

A. CALCULATIONS FOR COLUMN EXPERIMENTS

Adsorption columns were set up to receive some inlet concentration of Ca(OH)_2 at a specific flow rate. After contact of this solution with product for some time, a sample of known volume was taken and measured titrimetrically for concentration of Ca(OH)_2 . Adsorption of Ca(OH)_2 by a given weight of product was obtained over some specific time lengths. Integration of the curve C_o/C_i vs. time gave the total adsorption capacity for the amount of product used. Equations used are as follows:

$$\text{Amount } \text{Ca(OH)}_2 \text{ adsorbed, } x, \text{ in g} = Qt(C_i - C_o) \quad (\text{B.1})$$

where

x = amount adsorbed, gram Ca(OH)_2 ,

t = time elapsed, seconds,

C_i = inlet concentration, gram Ca(OH)_2 /liter,

C_o = outlet concentration, gram Ca(OH)_2 /liter.

$$\text{Total amount adsorbed, } q_e, \frac{\text{g Ca(OH)}_2}{\text{g product}} = \sum_i^N x_i \quad (\text{B.2})$$

B. CALCULATIONS FOR CONCENTRATION

A known volume of sample was titrated with standardized acid (HCl) of known normality. The following equation was used:

$$\frac{\text{g} \cdot \text{mole Ca(OH)}_2}{\text{liter}} = \frac{\text{meq HCl (to P-ind.)} - \text{meq HCl (P-ind. to BCG)}}{2(\text{ml Ca(OH)}_2 \text{ sample})} \quad (\text{B.3})$$

where

$$\text{meq HCl} = \text{miliequivalent HCl} = \frac{\text{miliequivalent}}{\text{ml}} \times \text{ml HCl used,}$$

P-ind. = phenolphthalein indicator,

BCG = bromocresol green methyl red indicator.

From the above equation g Ca(OH)_2 /L was obtained by multiplying by molecular-weight of Ca(OH)_2 (i.e., 74).

C. CALCULATIONS FOR EQUILIBRIUM EXPERIMENTS

In conducting equilibrium experiments a known weight sample of product was contacted with known volume of Ca(OH)_2 at an initial saturation concentration. After some time solutions were filtered out and titrated with acid. Equation B.3 was used for getting the concentration. The difference between initial and final concentration was multiplied by the amount of solution in contact with product to obtain the capacity of that amount of product. Division by the number of grams product used gave q_e for equilibrium experiments. For complete

mix conditions capacities of each test were added as in Equation A.2 to find the total capacity.

VITA

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